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CALIFORNIA UNIV BERKELEY DEPT OF CHEMISTRY
CROSSED MOLECULAR BEAM STUDY OF THE REACTIONS OF OXYGEN AND FLU--ETC
MAR 81 Y T LEE
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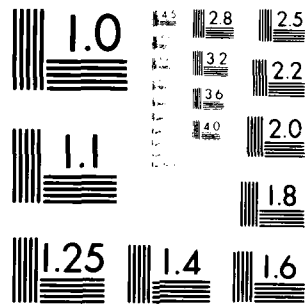
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<p>There has been a shift in the direction of this research program during the past year. In order to understand the dynamics of unimolecular dissociation of isolated molecules, a new program on molecular beam photofragmentation translational spectroscopy was initiated.</p> <p>Three projects which have been completed during the last year are summarized</p> <ol style="list-style-type: none"> 1. On the Photodissociation of Nitromethane at 266 nm. 2. Energy Splitting Between Singlet and Triplet Methylene by Photodissociation of Ketene. 3. Frequency Dependence of Quantum State Distributions of Photofragments of Ozone. <p>All three projects involve the dissociation through electronic excitation. In the coming years, the dynamics of dissociation of energetic molecules through ground electronic states will be investigated using infrared multiphoton excitation processes.</p>					

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I. Progress Report (January 1, 1980 to March 31, 1981)

Crossed Molecular Beam Study of the Reactions of Oxygen Atoms
and Fluorine Atoms.

N00014-75-C-0671

Principal Investigator: Yuan T. Lee

A. INTRODUCTION

There has been a major shift of the direction of this research program in the past year, although the title of this contract has not changed.

With the consent of Dr. R. S. Miller, Power Division, a new program on photodissociation translational spectroscopy was initiated. Three systems which have been studied and will be summarized in this report are:

- 1) On the Photodissociation of Nitromethane at 266 nm.
- 2) Energy Splitting Between Singlet and Triplet Methylene by Photodissociation of Ketene.
- 3) Frequency Dependence of Quantum State Distributions of Photofragments of Ozone.

All three studies were carried out with our new high resolution crossed molecular beams apparatus with a Nd-YAG laser (frequency quadrupled) or a rare gas halides excimer laser replacing one of the molecular beam sources. These studies on photofragmentation also represent the initiation of the investigation of the dynamics of photodissociation and unimolecular decomposition of polyatomic molecules, especially, those related to the energetic materials.

B. On the Photodissociation of Nitromethane at 266 nm.

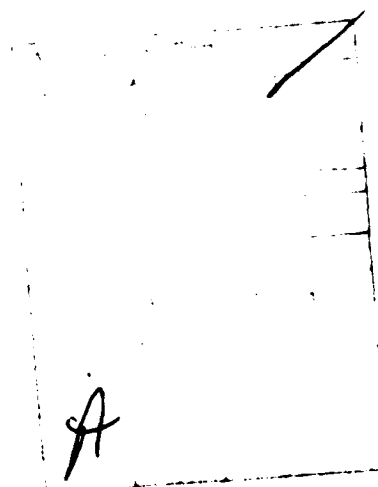
H. S. Kwok, G. Z. He, R. K. Sparks, and Y. T. Lee

INTRODUCTION

Nitromethane is one of the high yield clean liquid fuels. Its detonation characteristics have been studied quite extensively.¹ Recently, there has also been some interest in the photodissociation of nitromethane because of a possible important role in atmospheric chemistry. The absorption spectrum of nitromethane in the UV region consists of a main band peaking at 190 nm with a relatively large cross section of $\sim 2 \times 10^{-17} \text{ cm}^2$ and a much weaker band at around 270 nm with almost a 600 times smaller cross section.²⁻⁴ The transition is believed to be a $n \rightarrow \pi^*$ transition into a $\text{NO}_2 \pi$ orbital. A quantum yield of unity was often assumed for dissociation over this entire absorption range in view of the continuous nature of the absorption spectrum. A recent estimate of the atmospheric photodissociation lifetime of nitromethane was based on this assumption.²

However, in an earlier study of the photodissociation of nitromethane in liquid using 266 nm picosecond pulses, it was found that the production of NO_2 seemed to increase linearly in time after an induction period of several nanoseconds after the laser pulse.⁵ This apparent abnormal behavior was in line with the suggestion that the photodissociation of CH_3NO_2 at 266 nm is indirect⁶ and raised the question of quantum yield and primary dissociation mechanism in the weaker absorption band around 270 nm.

We have performed a study of the photodissociation of nitromethane and nitromethane clusters in a crossed laser-molecular beam apparatus. Our purpose was to clarify whether the previously reported photodissociation of nitromethane at 266 nm can actually take place under collision free conditions. If the excitation of isolated nitromethane is not a direct photodissociation transition and does not dissociate appreciably under collision free conditions, then it would be interesting to investigate whether the intramolecular dissociation will be facilitated by the presence of other nearby molecules. This possible process was investigated by exciting small (2 or 3 molecules) clusters of CH_3NO_2 produced in a supersonic expansion. The cluster could either decay by perturbation induced fragmentation of the CH_3NO_2 molecules, or by dissociation of the van der Waals bonds holding the clusters together.



EXPERIMENTAL

The crossed laser-molecular beam machine with a rotatable mass spectrometric detector used in this experiment was similar in design to an older machine⁷ and has been described in detail elsewhere.⁸ Its distinguishing characteristics are a much higher resolution in time-of-flight velocity measurements due to a longer flight path, much lower detector background levels, and a wider angular scanning range. It has been successfully applied to a study of the photodissociation of ozone, in which the vibrational states of the O_2 photofragment product were clearly resolved.⁹

The laser source used in this experiment was the fourth harmonic frequency of the Nd:YAG laser. Typically 50 mJ of energy per pulse at 266 nm was used. The laser pulse duration was about 7 ns and the repetition rate was 10 pps. In order to collect signal for 30,000 laser shots, a typical run lasted for one hour. The central feature of the detection system is a very fast 255 channel scaler triggered by the laser pulse with negligible delay.⁸

The molecular beam of nitromethane was produced by a supersonic expansion of a mixture of nitromethane with a rare gas carrier through a 0.23 mm diameter quartz nozzle. The temperature of the nozzle was controlled externally by a resistive heater. The gas mixture was formed by bubbling the carrier gas, either argon or helium, through a bottle of liquid nitromethane immersed in a constant temperature bath. The temperature of the bath was adjusted to control the partial pressure of the nitromethane.

In the molecular beam photofragmentation experiments where the yield of photodissociation products are expected to be low, it is possible to enhance the detectability of the dissociation products, with the sacrifice of angular and velocity resolution, by increasing the laboratory velocity of the molecular beam. If the velocity of the molecules in the beam could be increased to a value which is substantially larger than the velocity of the product in the center-of-mass coordinate, the product would be confined in a relatively small forward cone in the laboratory frame. We tried to accomplish this by both raising the nozzle temperature and seeding 35 torr of nitromethane in 400 torr of helium gas in the supersonic expansion. At a nozzle temperature of 100°C, excessive formation of molecular clusters was prevented, the velocity of the nitromethane molecules was found to be 1.55×10^5 cm/s. By changing the expansion conditions of the nozzle, namely, seeding 35 torr of nitromethane in 175 torr of argon in a room temperature nozzle, we were able to produce dimers, trimers and some higher polymers of CH_3NO_2 in the molecular beam. The velocity of trimers under this expansion condition was 0.56×10^5 cm/s.

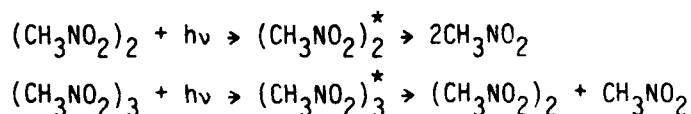
RESULTS AND DISCUSSION

After an intensive search for the most likely photodissociation products; CH_3 and NO_2 at masses 15 (CH_3^+), 46 (NO_2^+), no signal was observed even after accumulating for over 40,000 laser shots. Signals were also checked for less likely dissociation channels at masses 30 (NO^+), 31 (HNO^+) and 45 (CH_3NO^+), but again, no evidence of dissociation was found at any of these mass numbers. Detector angles were set at 20° and 30° from the molecular beam in our search for signal. According to a velocity diagram using the molecular beam velocity and the c.m. translational recoil velocity of the fragment for a given product translational energy, dissociation products should reach these laboratory detector angles, even if a large fraction of excess energy of 45 kcal/mole appears as internal excitation of products. For CH_3 and NO_2 , the required product translational energies are only 0.1 and 0.9 kcal/mole respectively at a laboratory angle of 20° and 0.2 and 2.0 kcal/mole respectively at 30° .

According to an estimate of the sensitivity of our detection system, commensurate with the integration time and the intensity of the molecular beam, the minimum detectable dissociation cross section is approximately 10^{-21} cm^2 if the molecule dissociates with a lifetime shorter than 10^{-5} second, which is the transit time of the molecules passing through the viewing zone of the detector. This estimate is also in agreement with the results of ozone and ketene photofragmentation experiments which have been successfully performed using this apparatus.¹⁰ The published absorption cross section for nitromethane is around $3 \times 10^{-20} \text{ cm}^2$ at

266 nm.^{2,11} Therefore, the apparent conclusion is that nitromethane excited at 266 nm does not photodissociate directly. Namely, the dissociation lifetime must be much longer than 10^{-5} seconds under collision free conditions.

Crossing the laser (266 nm) with the molecular beam containing small fractions of dimers and trimers of nitromethane, signals due to laser excitation were observed at mass 61 (CH_3NO_2^+) and 122 ($\text{CH}_3\text{NO}_2)_2^+$. These signals were due to the following vibrational predissociation processes of vibronically excited molecular clusters.



These predissociations occur because the excitation energy in the vibrational degrees of freedom in the cluster is larger than the binding energy between components of the cluster. Similar predissociations have been observed via infrared vibrational excitation in clusters of benzene, ammonia, methanol, water and hydrogen fluoride.¹² Figure 1 and Fig. 2 show the angular and velocity distributions of the product detected as $(\text{CH}_3\text{NO}_2)_2^+$. The solid lines passing through the data points in both figures represent the result of a theoretical fit calculated using a translational energy distribution shown in Fig. 3. The dotted curve in Fig. 2 represents the velocity distribution of the nitromethane trimers before dissociation. We can see that the extra translational energy in the fragments broadens the velocity distribution considerably.

From Fig. 3, it is clearly seen that the maximum translational energy in the predissociation product is about 1 kcal/mole. However, most of the product fragments prefer to have no excess kinetic energy. This observation is almost identical to the results on the infrared predissociation of benzene clusters.¹³

The observation of strong predissociation signal from the clusters also points to the conclusion that the lack of signal from the photodissociation of CH_3NO_2 experiment is indeed a real indication that CH_3NO_2 excited by 266 nm does not dissociate directly. And, as we have mentioned above, it implies an upper limit of 10^{-21} cm^2 for the direct photodissociation cross section of CH_3NO_2 . Since the corresponding absorption cross section is $3 \times 10^{-20} \text{ cm}^2$, this absorption must be due to a bound-bound transition. The observation of NO_2 fragments in all previous bulk experiments on nitromethane must be due to collisional dissociation of the excited molecules. At atmospheric pressure, collisional relaxation and/or collision induced intersystem crossing should compete with collisional dissociation and the assumption of a quantum yield of unity in the weaker absorption band peaking at 270 nm is clearly not justified. Since the excitation energy at 266 nm is much larger than the dissociation energy of $\text{CH}_3\text{NO}_2 \rightarrow \text{CH}_3 + \text{NO}_2$, lack of direct dissociation signal implies either an intersystem crossing for the excited singlet state, so that the effect of photoexcitation at 266 nm might result in a bound metastable triplet state with some vibrational excitation, or an extremely long predissociation lifetime.

Collision induced processes cannot be important for monomers in the molecular beam, however, all of them are, in principle, possible processes in the clusters. Apparently, in dimeric or trimeric clusters of nitromethane, "collision induced" chemical dissociation does not seem to compete efficiently with vibrational predissociation processes. The identity of the electronic state from which the system predissociates is not determined by our experiment and certainly presents an interesting question. Also, the predominance of vibrational predissociation in the cluster suggests, but does not necessarily imply, that vibrational relaxation of the excited electronic state will be the major process in room temperature collisions. The very low internal temperature of the cluster requires that it samples a much more restricted region of the interaction potential than would occur in a normal collision. An investigation of the relative importance of vibrational relaxation and collision induced dissociation as a function of collision energy would be very interesting, as would its dependence on the vibrational energy of the excited electronic state.

ACKNOWLEDGMENT

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FIGURE CAPTIONS

Fig. 1. Laboratory angular distributions of $(\text{CH}_3\text{NO}_2)_2$ from vibrational predissociation of vibronically excited $(\text{CH}_3\text{NO}_2)_3$ at 266 nm excitation. Dots are experimental results. The solid curve is the calculated angular distribution using the energy distribution of Fig. 3.

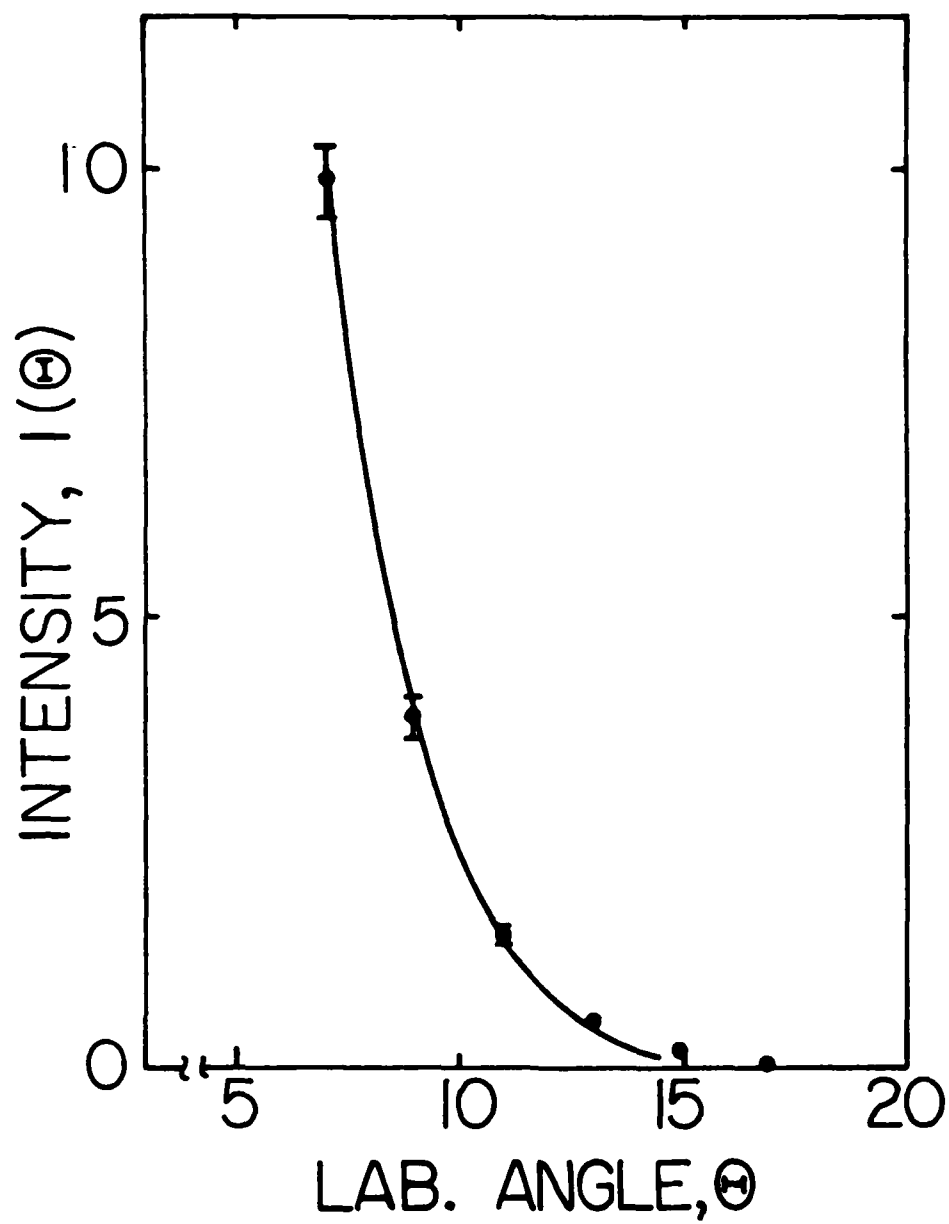
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Fig. 2. Laboratory velocity distributions of $(\text{CH}_3\text{NO}_2)_2$ from $(\text{CH}_3\text{NO}_2)_3$. Symbols are the same as indicated in Fig. 1. Dashed curve is the velocity distribution of $(\text{CH}_3\text{NO}_2)_3$.

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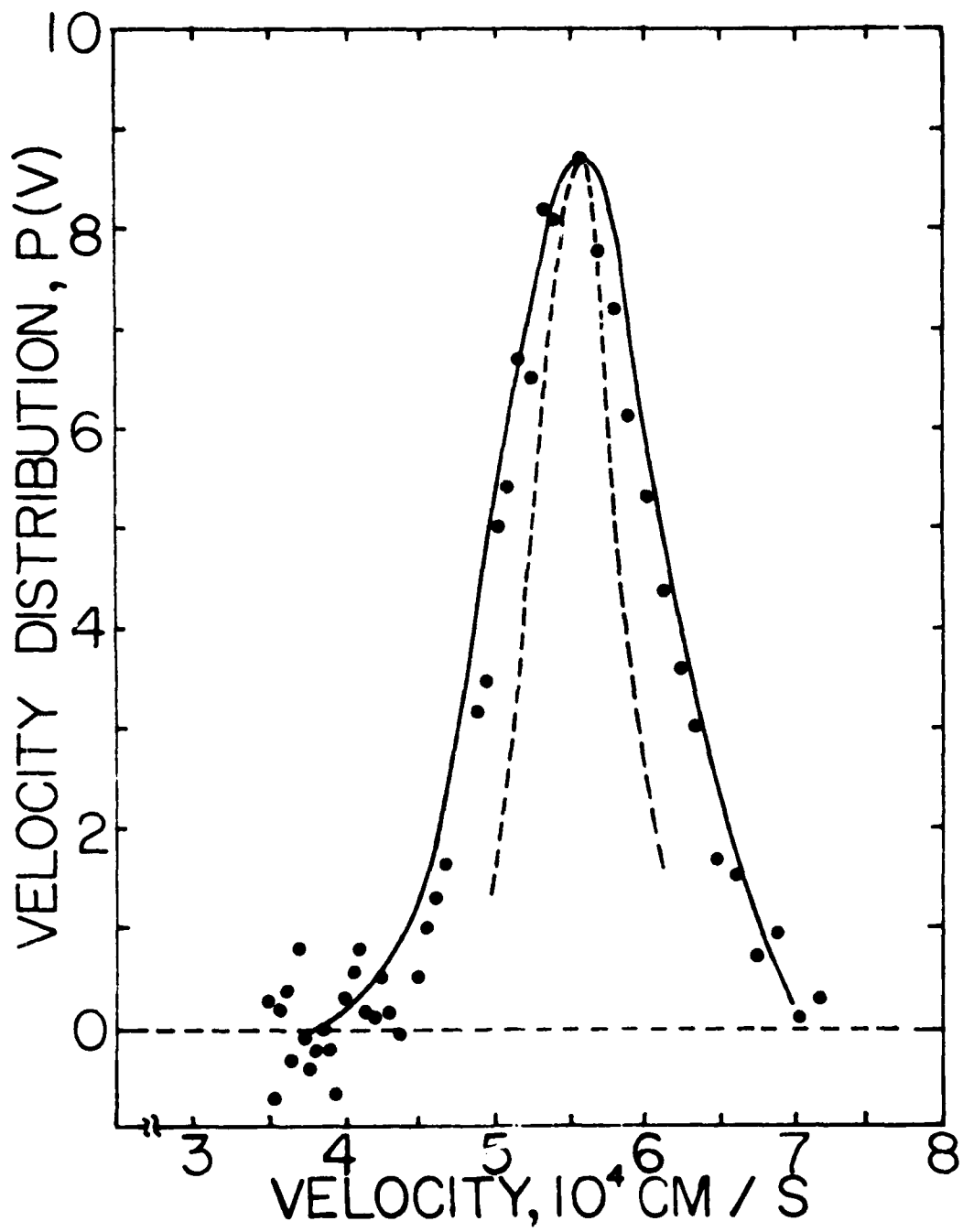
Fig. 3. Translational energy distribution of the process $(\text{CH}_3\text{NO}_2)_3 \xrightarrow{266 \text{ nm}} (\text{CH}_3\text{NO}_2)_2 + \text{CH}_3\text{NO}_2$ which gives the best fit to the data shown in Fig. 1 and Fig. 2.

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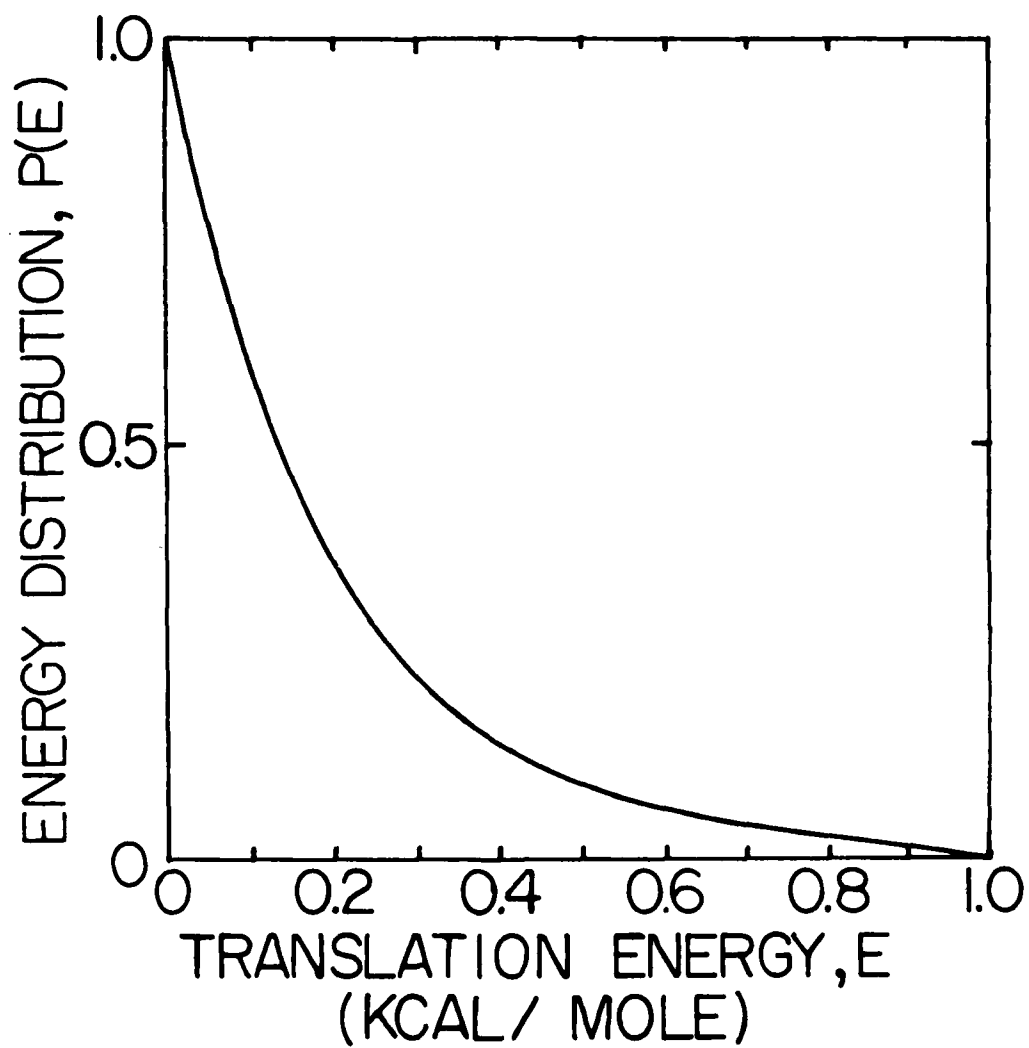
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Fig. 1



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FIG. 2



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Fig. 3

C. Energy Splitting Between Singlet and Triplet Methylene by Photodissociation of Ketene.

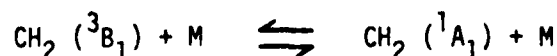
C. C. Havden, D. M. Neumark, R. K. Sparks, and Y. T. Lee

INTRODUCTION

The unique chemistry of the methylene, CH_2 , radical is primarily due to the substantially different chemical behavior of two low lying electronic states, the ground ($^3\text{B}_1$) state and the lowest excited ($^1\text{A}_1$) state. The photochemical processes commonly used to produce CH_2 can yield both states, and the nature of subsequent reactions depends on whether triplet or singlet methylene is involved. In spite of a large number of experimental and theoretical studies questions about the energies of these states still remain.

Several different experimental approaches have been used to obtain information on these energies. Most of the results are consistent with a singlet-triplet splitting of about 8.5 ± 1 kcal/mole, but the most direct measurement, the photoelectron spectrum of photodetachment from CH_2^- gives 19.5 kcal/mole.¹ In addition, the best calculations show the energy difference to be 10.5 ± 2 kcal/mole, supporting the lower experimental value. The molecular beam photofragmentation translational spectroscopy on ketene described in this paper provides another microscopic experiment which eliminates many of the problems associated with other methods, and thus should help resolve the differences between the experimental results.

Measurements of the temperature and pressure dependence of product ratios from CH_2 ($^1\text{A}_1$) and CH_2 ($^3\text{B}_1$) reactions have been used to estimate the singlet-triplet energy difference assuming the reaction



maintains equilibrium concentrations of the two species. Values of -5 ± 0.7 kcal/mole² and 8.7 ± 0.8 kcal/mole³ were then obtained. To determine the heat of formation of CH₂ (³B₁), the threshold for production of CH₂⁺ from dissociative photoionization has been measured using several different precursors. From known enthalpies of formation for the dissociating molecules, and the ionization potential of CH₂, an upper limit can be placed on ΔH_{fo}^0 CH₂ (³B₁). This will be the correct value if no excess energy is released in the dissociative photoionization at threshold. The enthalpy of formation of methylene (³B₁) from this procedure ranges from 91.9 to 95.5 kcal/mole with the best values being 93.8 ± 0.4 and 93.4 ± 0.4 kcal/mole from photoionization of methane and ketene respectively⁴ and 94.6 ± 0.5 kcal/mole from methane.⁵ The spread in these numbers can be accounted for by the difficulty in determining the thresholds, and in estimating the contributions of internal energy to the process. Recent work has also placed an upper limit on ΔH_{fo}^0 CH₂ (¹A₁). The internal excitation of methylene (¹A₁) produced from photodissociation of ketene with a nitrogen laser was determined by laser induced fluorescence. The temperature dependence of the fluorescence intensity from CH₂ was measured to estimate the amount of internal excitation that must be present in ketene for dissociation to occur at the nitrogen laser wavelength (337.1 nm). Then from the heats of formation of CH₂CO and CO, ΔH_{fo}^0 CH₂ (¹A₁) can be calculated, with the result.⁶

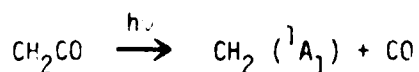
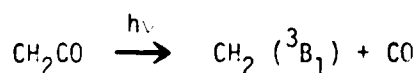
$$\Delta H_{fo}^0 \text{ CH}_2(^1\text{A}_1) = 101.7 \pm 0.5 \text{ kcal/mole.}$$

This upper limit should be close to the correct value if the internal energy in the CO fragment and the kinetic energy release are negligible.

In a very similar experiment the threshold for CH_2 ($^1\text{A}_1$) production from ketene photodissociation was measured by monitoring methylene laser induced fluorescence as a function of photolysis laser wavelength. An upper limit of

$$\Delta H_{f0}^0 \text{CH}_2 (^1\text{A}_1) = 101.9 \pm 0.5 \text{ kcal/mole}$$

was determined.⁷ The wavelength threshold for ketene photolysis at 298°K to CH_2 ($^3\text{B}_1$) and CO has also been determined from the appearance of CO product. In the same experiment the threshold for ketene photolysis to give CH_2 ($^1\text{A}_1$) was measured from the products of the singlet reacting with cis-2-butene. Thus enthalpies for the reactions



were determined at 298°K. The difference in the threshold energies then gave a value of $8.3 \pm 1 \text{ kcal/mole}$ for the singlet-triplet energy splitting.⁸

The studies mentioned above and many other similar experiments are all consistent with a $\text{CH}_2 (^3\text{B}_1) - \text{CH}_2 (^1\text{A}_1)$ splitting of 8.5 ± 1 kcal/mole, but the most direct observation of the splitting, the photoelectron spectrum from the photodetachment of CH_2^- to produce $\text{CH}_2 (^1\text{A}_1)$ and $\text{CH}_2 (^3\text{B}_1)$ has been interpreted to show a splitting of 19.5 or 23.2 kcal/mole.¹ There are several possible explanations for this apparent contradiction. If the singlet-triplet splitting is indeed about 8.5 kcal/mole, then the photoelectron spectrum is not correctly assigned, and perhaps hot bands of CH_2^- are being observed. Franck-Condon factors for the photodetachment of an electron from CH_2^- , have been calculated from ab initio potential curves, and fit the observed spectra well if it is assumed that hot bands are present.^{9,10} This assignment predicts a $^1\text{A}_1 - ^3\text{B}_1$ splitting of 9 ± 1 kcal/mole, but extensive experimental work attempting to confirm the presence of hot bands has tended to show that the observed features are not due to vibrationally excited CH_2^- . If the methylene singlet-triplet splitting is actually around 20 kcal/mole, then it is difficult to explain the photochemical and photoionization results. An upper bound for $\Delta H_{\text{fo}}^0 \text{CH}_2 (^1\text{A}_1)$ is firmly established, within the accuracy of the corrections for the effects of reactant internal excitation to photodissociation (± 1 kcal/mole). Thus for the splitting to be as large as 20 kcal/mole the apparent thresholds in the photolysis and dissociative photoionization experiments used to determine $\Delta H_{\text{f}} \text{CH}_2 (^3\text{B}_1)$ must be 11.5 kcal/mole higher than the actual thermodynamic limit and this

amount of excess energy must be released at the threshold. The reduction of the heat of formation of CH_2 ($^3\text{B}_1$) by as much as 10 kcal/mole is also not compatible with the results of many chemical activation studies of unimolecular decomposition.¹¹

Many theoretical studies of methylene energy levels have been performed, and the best ab initio calculations have given the values 10.4 ± 2 kcal/mole¹² and 10.6 kcal/mole^{13,14} for the singlet-triplet splitting. There is still a question of the exact correction to these calculations necessary to account for the differences in zero point energy of the two states. Harding and Goddard⁹ calculated total zero point energies using the harmonic approximation and found a very small (0.16 kcal/mole) difference between the singlet and triplet. The result (10.4 kcal/mole) was corrected for this effect. Thus the theoretical results tend to support the lower (8.5 kcal/mole) experimental value for the splitting but do not accurately agree with it.

By detecting the products of the photofragmentation of ketene in a molecular beam experiment, many of the uncertainties in other measurements of the methylene singlet-triplet splitting can be avoided. Most importantly the velocity of the fragments can be directly measured and the translational energy distribution determined. The maximum translational energy released in the dissociation should correspond to the production of ground state CH_2 and CO, and even if there is an exit barrier for dissociation, the potential energy barrier will be

transformed into product translational and internal energy. A further advantage is that the expansion which produces the molecular beam cools the ketene sufficiently that its internal energy can be neglected.

EXPERIMENTAL

Ketene was prepared by pyrolysis of acetic anhydride and trapped at 77°K. A portion was purified for use each day by trap to trap distillation. A supersonic beam of ketene seeded in helium was produced by bubbling helium through liquid ketene in a dry ice-ethanol bath, and expanding the resulting mixture at 300 torr through a 9 mil nozzle. After passing through two stages of differential pumping and collimation the beam, with a spread of 2.5°, enters the interaction chamber where the pressure is maintained at about 1×10^{-7} torr. The beam of ketene had a peak velocity of 1.12×10^5 cm/sec and a full width at half maximum velocity spread of about 10%. The density of ketene in the interaction region is about 10^{11} molecules/cc.

A Lumonics Model TE-861 rare gas halide excimer laser was used at 351 nm (XeF) and 308 nm (XeCl) for the photodissociation. The laser beam was focused to a spot of about 0.5 cm diameter where it crossed the molecular beam and was operated at 70 Hz with a measured average power of about 2.5 watts with both XeF and XeCl.

The photofragments produced pass through an entrance slit of the detector and two stages of differential pumping then enter the ionization chamber where they are ionized by electron impact. An Extranuclear quadrupole mass spectrometer provides mass selection, and a Daly detector is used to count the ions. The entire detector assembly can be rotated around the laser-molecular beam crossing point, detecting products as a function of angle with a resolution of 2.5°. Neutral products travel a distance of 34.1 cm

to the ionizer after the dissociation. The flight time from the interaction region to the detector, starting with the laser pulse, was recorded by a multichannel scaler. The resulting time of flight spectra were stored on floppy disk for later analysis.

RESULTS AND ANALYSIS

The data obtained in this experiment consist of time of flight distributions which are proportional to the number density of the detected product present in the mass spectrometer ionizer as a function of time after the laser pulse. To determine the thermochemical quantities of interest the data must be converted to energy distributions in the center of mass coordinate system of the dissociating molecule. Figure 1 shows a velocity vector diagram for the process. The origin of the lab coordinate system is the base of the beam velocity vector and lab angles are measured from the direction of the beam. The tip of this vector defines the origin of the center of mass coordinate system and the circles show CO fragment velocities corresponding to various product translational energies.

It was found necessary to make a small background correction to the raw data, as a result of the large detector apertures used to enhance the signal to noise ratio in this experiment. These large apertures allow some product molecules to strike surfaces of the ionizer and raise the background for a short time after each laser pulse. The background then decays exponentially with a time constant determined by the pumping speed for that molecule. Correction for this minor effect is made by requiring the background for times where signal cannot appear due to kinematic constraints to be equal to the background before the first signal arrives. The behavior of the time dependent background is simulated with an amplitude which is proportional to the intensity of signal, and a decay constant which

roughly corresponds to the pumping speed, and then subtracted from the data. These two parameters can be varied until the proper background level is obtained. An example of original and corrected data is shown in Fig. 2. All further CO data shown in Figs. 3 and 5 has been corrected in this manner. The problem does not appear for CH_2 , apparently because it is rapidly destroyed by wall collisions.

The determination of the center of mass energy distribution is done by an iterative process. A trial energy and angular distribution is used as the input to a computer simulation program. The energy distribution is converted to center of mass velocity flux according to the relation:

$$I_{\text{c.m.}}(u, \theta_{\text{cm}}) = u I_{\text{cm}}(E_{\text{cm}}, \theta_{\text{cm}})$$

This is then transformed to laboratory time of flight.

$$N_{\text{LAB}}(t, \theta_{\text{LAB}}) \propto \frac{v^3}{lu^2} I_{\text{cm}}(u, \theta_{\text{cm}})$$

where l is the flight path, and v and u are lab and c.m. velocity respectively. The beam velocity and angular spreads are accounted for by summing the contributions due to different initial speeds and angles. The detector resolution is included in a similar fashion. The result for a given center of mass energy distribution was compared to the data, and the input changed until the agreement was satisfactory.

An energy distribution was chosen for each laser frequency used which most closely fit all the data taken at different angles. The distributions had the general form

$$P(E) = C(E - E_l)^{\alpha} (E_T - E)^{\beta}$$

For convenience in fitting the data the actual parameters used in the computer simulation were E_p , the energy at which the distribution peaks; $E_p - E_l$, the difference between the peak and the low energy at which the probability goes to zero; and $E_T - E_p$, the difference between the high energy where the probability goes to zero and the peak. The parameter α can then be calculated

$$\alpha = \frac{\beta(E_p - E_l)}{E_T - E_p}$$

Several distributions could be added together to produce the best fit to the data.

The results for the XeF laser at 351 nm are shown in Fig. 3. The fit (solid line) is superimposed on the data (solid dots). An angular distribution of $1 + \sin^2\theta$ produced the best agreement with the data. The time of flight for CO products could be fit with the same energy distribution at the two angles, but for the CH₂ product the entire distribution has to be shifted 0.5 kcal/mole to higher energy. For determining the thermodynamic quantities discussed later, the center of mass energies consistent with the data from the CO fragment were used since the signal to noise is much better than for the CH₂ fragment.

The energy distribution is shown in Fig. 4, and the actual values used for the parameters are shown in Table 1. Figure 3 also shows the result of calculations of the laboratory time of flight at 14° if the center of mass energies are shifted up and down by 1 kcal/mole without changing the energy distribution. This gives an idea of the sensitivity of the experiment. The results for the CO fragment when ketene is dissociated with the 308 nm light from the XeCl laser are shown in Fig. 5. All angles are fit with the same energy distribution as shown in Table 1, and an angular distribution $1 + \cos^2\theta$ was used. The energy distribution is shown in Fig. 6. Again the sensitivity to energy shifts of 1 kcal/mole are shown (Fig. 5) for a lab angle of 14° . Because of the larger product translational energy released at this frequency the sensitivity to the threshold energy distribution is less than that at 350 nm.

From the energy distributions determined in this experiment several thermochemical quantities related to ketene dissociation can be derived. The expansion producing the supersonic beam using He carrier gas cools the ketene sufficiently that it can be assumed the molecule starts essentially in its ground state. A photon of known energy is absorbed, and we then measure the translational energy of the fragments. Because the sum of the translational energy and internal energy is the excess energy available for dissociation, the fastest products detected should correspond to ground state CO and CH₂ formation. Several previous experiments^{6,7}

have shown that the threshold for CH_2 ($^1\text{A}_1$) production from ground state ketene is substantially above the energy supplied by a 351 nm photon, so the signal at this wavelength must be due entirely to CH_3 ($^3\text{B}_1$). From the distribution in Fig. 4 the highest translational energy observed in the products is 3.8 kcal/mole. When this is subtracted from the 81.4 kcal/mole supplied by the photon it gives a value of 77.6 kcal/mole for the bond dissociation energy of CH_2CO to CH_2 ($^3\text{B}_1$) and CO. Photons at 308 nm from the XeCl laser energetically could produce both singlet and triplet methylene, but we observed only singlet. If triplet products were produced they would be considerably faster than the fastest signal observed. Figure 7 shows a simulated time of flight spectrum from an energy distribution which is the same as that used to fit the data at 308 nm, except for the addition of a second distribution an energy corresponding to that expected for the triplet, as determined from the result at longer wavelength. The second distribution has a peak 10% as high as the peak of the singlet distribution. The actual data shows no similar features in the corresponding position. Thus the highest translational energy products are assumed to be ground vibrational and rotational state CH_2 ($^1\text{A}_1$) and CO. Subtracting the translational energy (6.7 kcal/mole) of these products from the laser photon energy of 92.8 kcal/mole results in 86.1 kcal/mole for the bond dissociation of ketene to produce CH_2 ($^1\text{A}_1$) and CO.

From the known heats of formation of CH_2CO ($\Delta H_{\text{fo}}^0 = -10.7$ kcal/mole)¹⁵ and CO ($\Delta H_{\text{fo}}^0 = -27.199$ kcal/mole),¹⁶ the heat of formation of CH_2 can be calculated

$$\begin{aligned}\Delta H_{\text{fo}}^0 (\text{CH}_2 \text{ } ^3\text{B}_1) &= 77.6 \text{ kcal/mole} + \Delta H_{\text{fo}}^0 (\text{CH}_2\text{CO}) \\ &\quad - \Delta H_{\text{fo}}^0 (\text{CO}) = 94.1 \text{ kcal/mole}\end{aligned}$$

$$\begin{aligned}\Delta H_{\text{fo}}^0 (\text{CH}_2 \text{ } ^1\text{A}_1) &= 86.1 \text{ kcal/mole} + \Delta H_{\text{fo}}^0 (\text{CH}_2\text{CO}) \\ &\quad - \Delta H_{\text{fo}}^0 (\text{CO}) = 102.6 \text{ kcal/mole}\end{aligned}$$

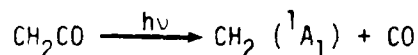
Thus the energy difference between the singlet ($^1\text{A}_1$) and triplet ($^3\text{B}_1$) states of CH_2 is 8.5 kcal/mole, with an uncertainty of approximately 0.8 kcal/mole, mainly from the experimental determination of the maximum translational energy release. These results are summarized in Fig. 8.

DISCUSSION

The value for the singlet-triplet splitting obtained from this work (8.5 kcal/mole) agrees very well with the lower value from previous experiments. The actual heats of formation derived from our results can also be compared with those previously determined.

The very close agreement of the photoionization value for ΔH_{f0}^0 (CH_2 $^3\text{B}_1$)^{4,5} with the number from our experiments, where translational energy release is observed directly, strongly supports the assumption that there is no excess energy release at the threshold of ionization. It also tends to confirm that the fastest products we observed from dissociation with 351 nm photons do correspond to ground vibrational state CO and CH_2 .

The threshold for the process



has been measured in several experiments. In the work of Lengel and Zare the value 85.2 ± 0.3 kcal/mole was obtained.⁶ The similar experiments of reference 7 yield 85.4 ± 0.3 . Simon and Curry found 84.0 ± 0.6 kcal/mole, for the process at 298°K. All of these determinations rely on the translational energy release being negligible at the threshold. Again the assumption seems to be valid as our value of 86.1 ± 0.5 kcal/mole agrees fairly well if the uncertainty in corrections of previous results for reactant internal energy is considered.

A large discrepancy exists between the results of this work, and the photodetachment results from CH_2^- , which support a large singlet-triplet splitting (19.5 kcal/mole).¹ As previously discussed, an upper limit can be placed on the energy of the CH_2 ($^1\text{A}_1$) state, so errors resulting in too small a value for the splitting must arise from placing the energy of the ($^3\text{B}_1$) state too high. If the photodissociation of ketene at 351 nm produces no ground vibrational state products then the value of $\Delta H_{\text{fo}}^{\text{O}} \text{CH}_2$ ($^3\text{B}_1$) determined in this experiment would be too high. This is very unlikely for several reasons. The heat of formation of triplet methylene we obtained agrees closely with previous measurements by completely different methods. It's difficult to imagine that identical errors appear in each case. In addition, if the splitting were as large as 19.5 kcal, then at least 15 kcal/mole is available to the products in the ketene dissociation at 351 nm. A maximum of 3.8 kcal appears as translation in our experiments. If there were at least another 11.0 kcal/mole of energy in the internal excitation of products, then the product vibrational states would be very highly inverted. This is not expected since the CO vibration and the CH_2 bending vibration both are strongly coupled to the reaction coordinate of the photodissociation of ketene.

There are several other interesting features of the center of mass energy distributions determined in this experiment. The shapes of the distribution of product energy at the two wavelengths are obviously very different. For the triplet (from 351 nm dissociation)

the product is fairly sharply peaked near the maximum translational energy release. The second smaller peak in Fig. 4 is necessary to fit the small feature in the time of flight data at 14° . The spacing between the two peaks is approximately equal to the energy of the bending vibration in ground state CH_2 (3.4 kcal/mole).¹ This suggests that a small fraction of the CH_2 is produced vibrationally excited. The translational energy distribution for singlet CH_2 production from 308 nm dissociation (Fig. 6) peaks at zero translational energy and is very broad. This shows that there is substantial internal excitation of the products. These results suggest that quite different processes occur at the two wavelengths, either two electronic states of ketene are involved, or the dissociation dynamics change between 351 nm and 308 nm. The difference between the angular dependence of the product intensity at the two wavelengths is further evidence that the dissociation process changes in this wavelength region, but due to the limited angular range covered in these measurements our data is not very sensitive to the angular distribution.

CONCLUSION

This paper has described the measurement of the energy splitting between the ground (3B_1) and first excited (1A_1) states of methylene. The experiment was especially designed to detect possible exit barriers to photodissociation which potentially could have caused errors in previous results. No evidence for such barriers was observed and our value of 8.2 kcal/mole agrees well with the majority of other experiments attempting to measure the singlet-triplet splitting.^{2,3,6,7,8} It is also in reasonable agreement with recent ab initio quantum mechanical calculations,^{12,13} but not with the larger value obtained from the photoelectron spectrum of photodetachment of CH_2^- .¹

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Table 1. Center of mass energy distribution parameters for the photodissociation of CH_2CO . Energies are in kcal/mole.

	E_p	$E_T - E_p$	$E_p - E_1$	β	Peak Height
351 nm dissociation product at 14° and 17°					
Fig. 4 High energy peak	2.3	1.5	1.2	2.5	1.0
Low energy peak	.45	.40	.40	1.3	.3
351 nm dissociation CH_2 product at 35°	2.8	1.5	1.2	2.5	1.0
308 nm dissociation CO product at 14°, 17°, 20° and 25°					
Fig. 6	0.0	6.7	0.0	1.2	1.0
Energy distribution for					
Fig. 7 Singlet	0.0	6.7	0.0	1.2	1.0
Triplet	9.2	6.0	4.8	2.5	0.1

FIGURE CAPTIONS

- Fig. 1. Newton diagram for photodissociation of CH_2CO showing relations between laboratory and center of mass velocities and angles. $V_{\text{CH}_2\text{CO}}$ and V_{CO} are laboratory velocity vectors, U_{CO} is a center of mass velocity vector. The origin of the lab coordinate system is the base of the vector for the initial CH_2CO velocity, and the origin for the center of mass system is the tip of the same vector. The circles have radii corresponding to the speed of the CO fragment in the center of mass frame for various amounts of translational energy release in the dissociation.
- Fig. 2. Time of flight data at a lab angle of 14° for the CO fragment from CH_2CO photodissociation at 308 nm. The dots are the original data, and the solid line shows the data after subtraction of time dependent background. $N(t)$ is the number of counts as a function of time (arbitrary units).
- Fig. 3. Time of flight data for fragments from ketene photodissociation at 351 nm and various lab angles. $N(t)$ is the number of counts per time channel (arbitrary units). Dots are the data, the solid lines are the fits. E_T is the highest center of mass energy (kcal/mole) with non-zero probability in the energy distributions used for the computer simulation. At 14° the energy distribution has been shifted ± 1 kcal/mole to show the sensitivity of the fits.

- Fig. 4. Center of mass energy distribution for ketene photofragmentation at 351 nm. The energy scale is in kcal/mole. This distribution was used to fit the data for the CO fragment at lab angles of 14° and 17° . The actual parameters are in Table 1.
- Fig. 5. Time of flight data for CO fragment from ketene dissociation at 308 nm. $N(t)$ is the number of counts per time channel (arbitrary units). Dots are the data, lines are the computer generated fits. Time of flight spectra have been calculated at 14° for the center of mass energy distribution with parameters shown in Table 1 and with E_T shifted ± 1 kcal/mole.
- Fig. 6. Center of mass energy distribution for ketene photodissociation at 308 nm. Energy scale is in kcal/mole. The distribution shown was used to fit all the CO time of flight data from the 308 nm dissociation. The parameters for this distribution are given in Table 1.
- Fig. 7. The dots show the time of flight data for the CO fragment at 14° from CH_2CO photodissociation with 308 nm light. The solid line is the computer calculated time of flight spectrum for CO fragments if a center of mass energy distribution corresponding to CH_2 ($^3\text{B}_1$) production at this wavelength is added to the distribution actually used to fit the data. The parameters used to generate this figure are shown in Table 1.

Fig. 8. Energy level diagram for the ketene photodissociation process. All energies shown are in kcal/mole.

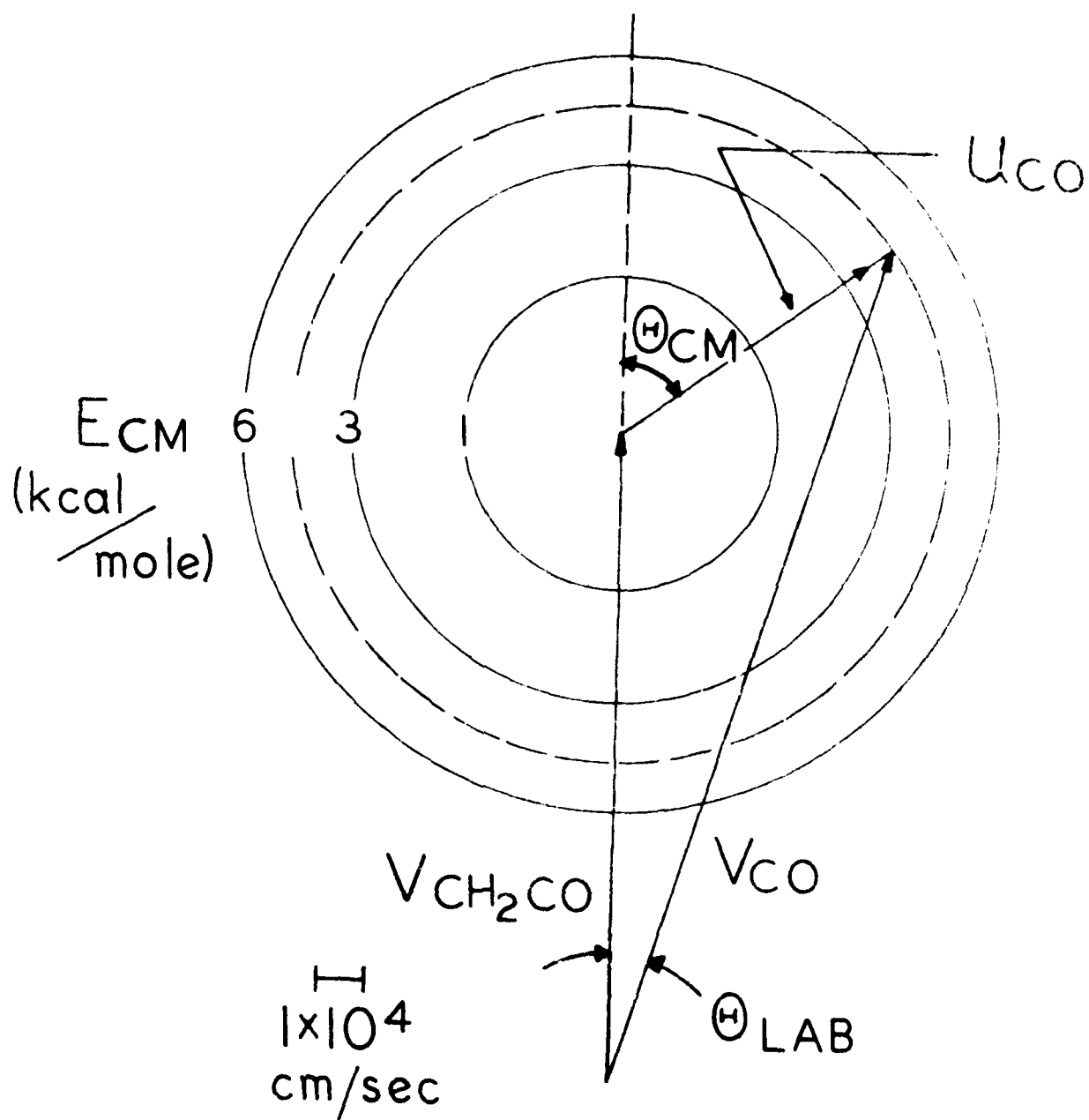


Fig. 1

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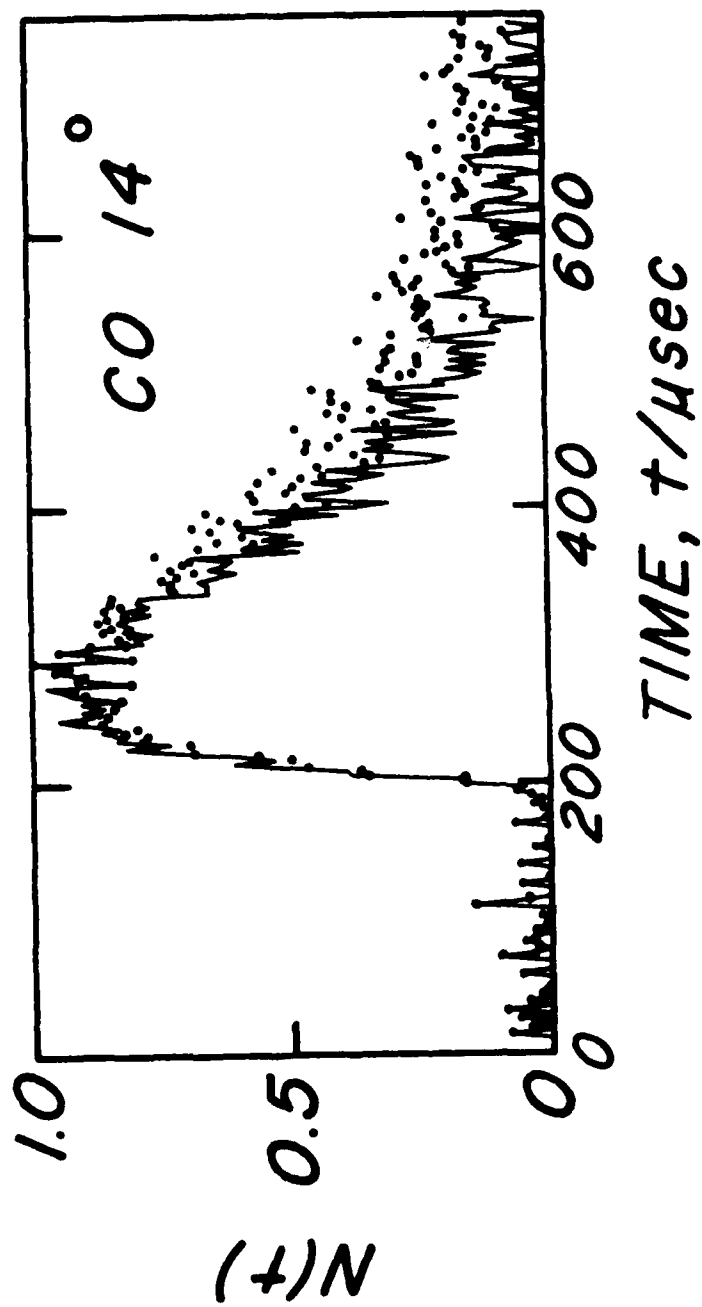


Fig. 2

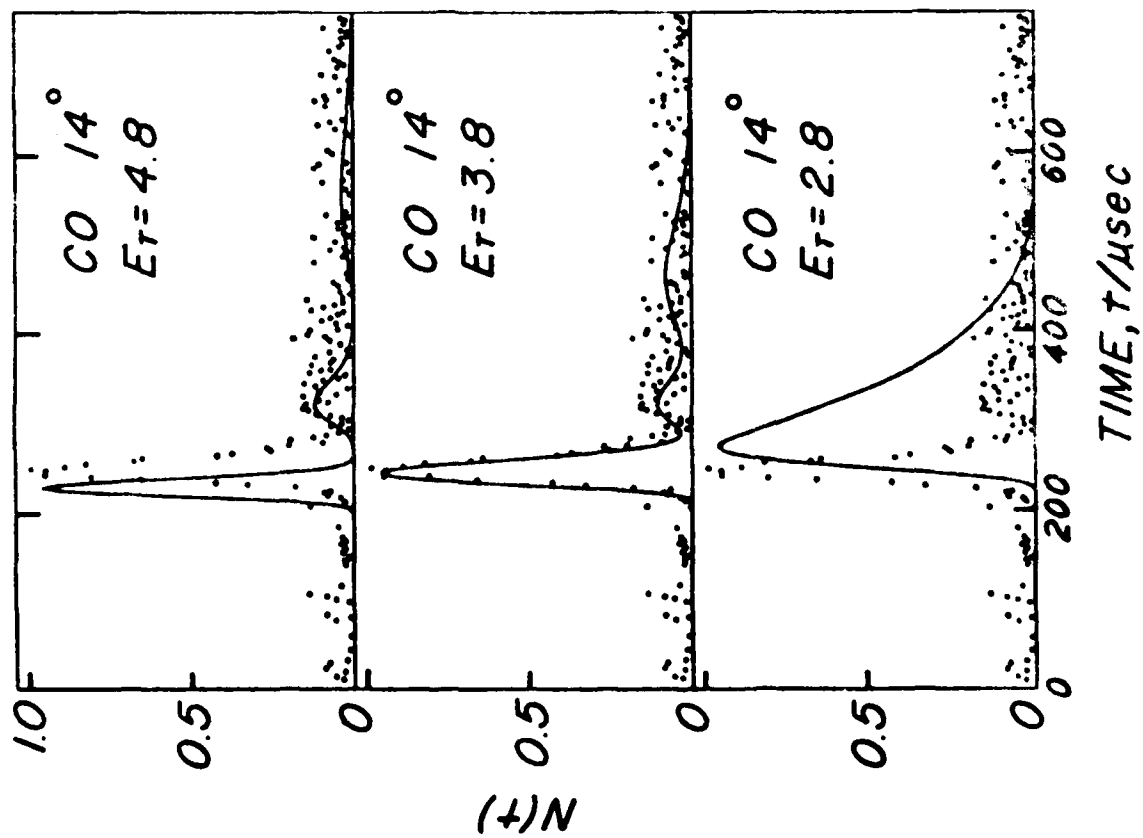


Fig. 3

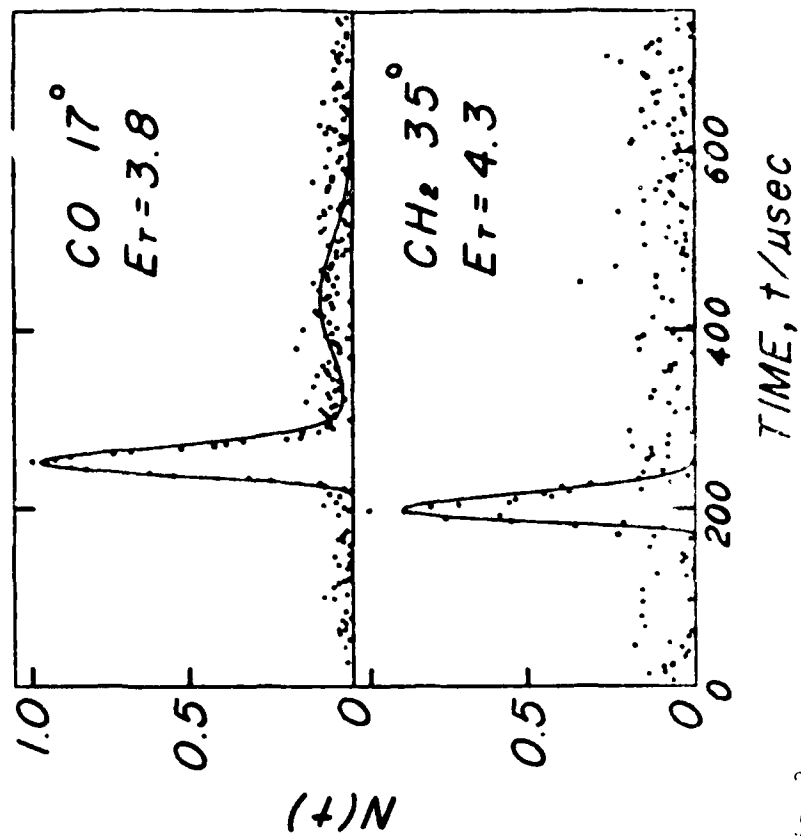
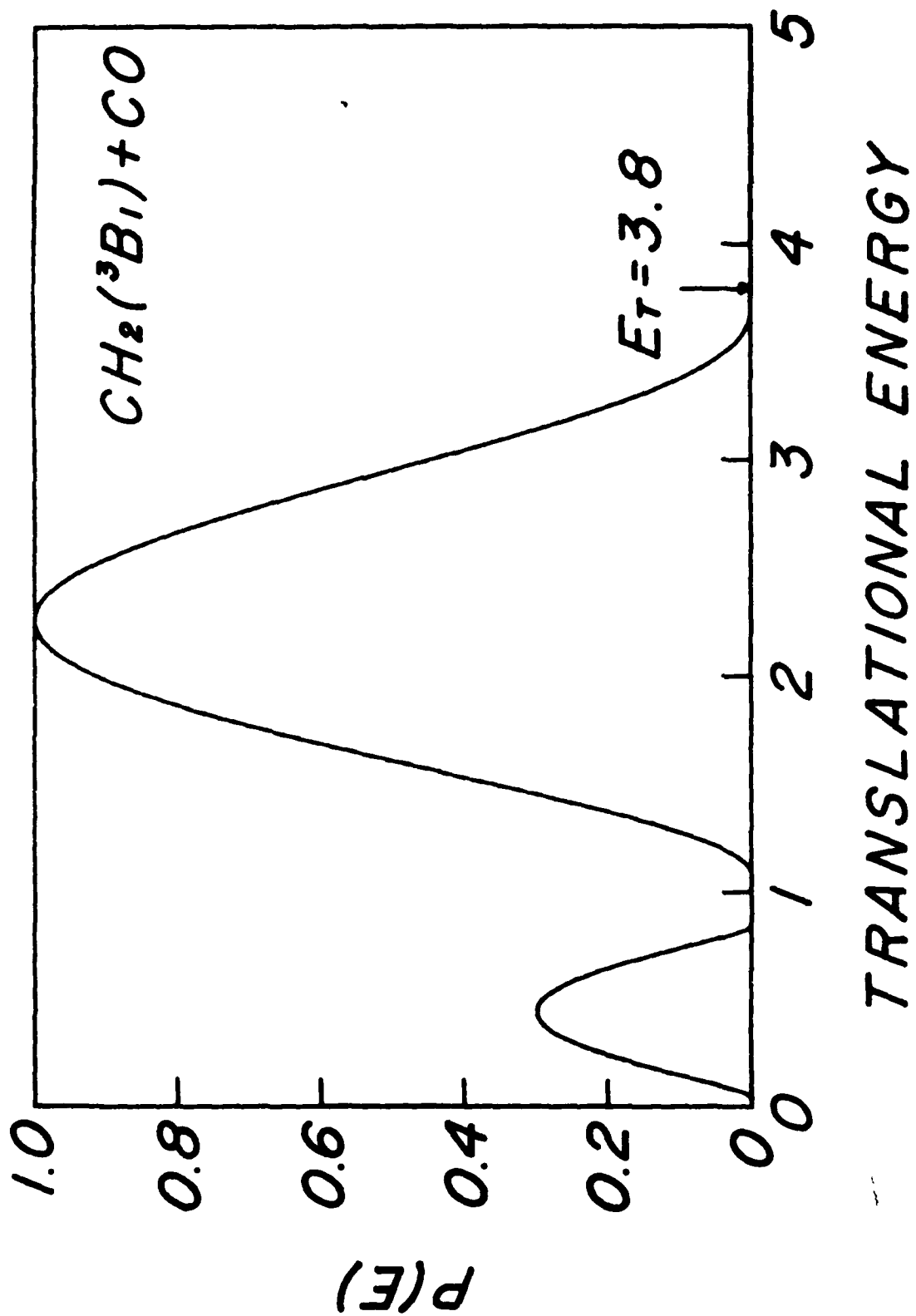
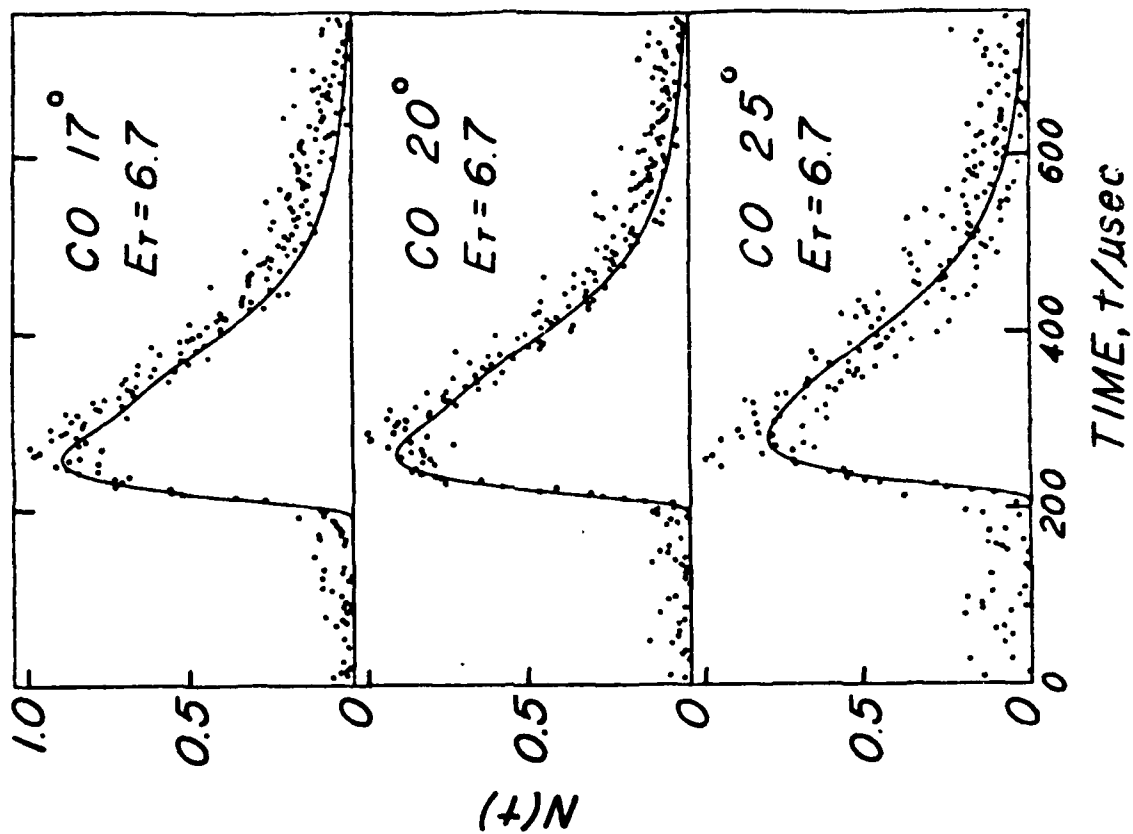


Fig. 3



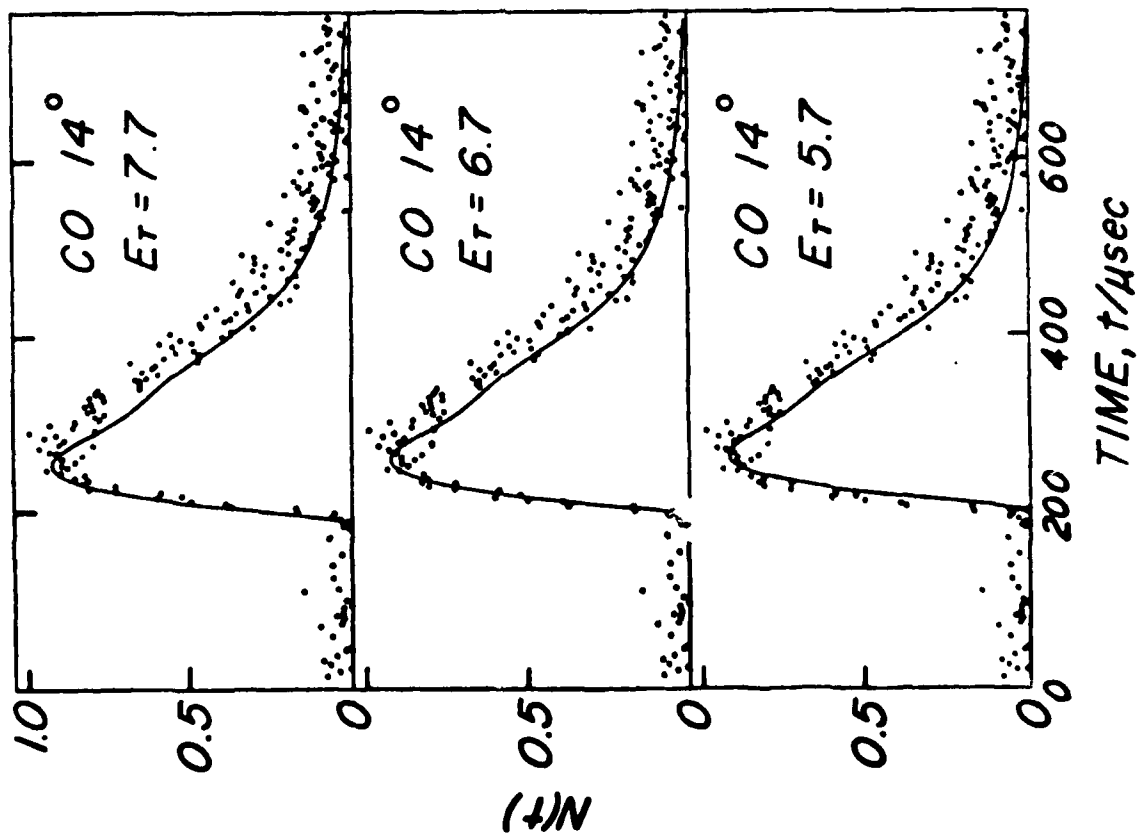
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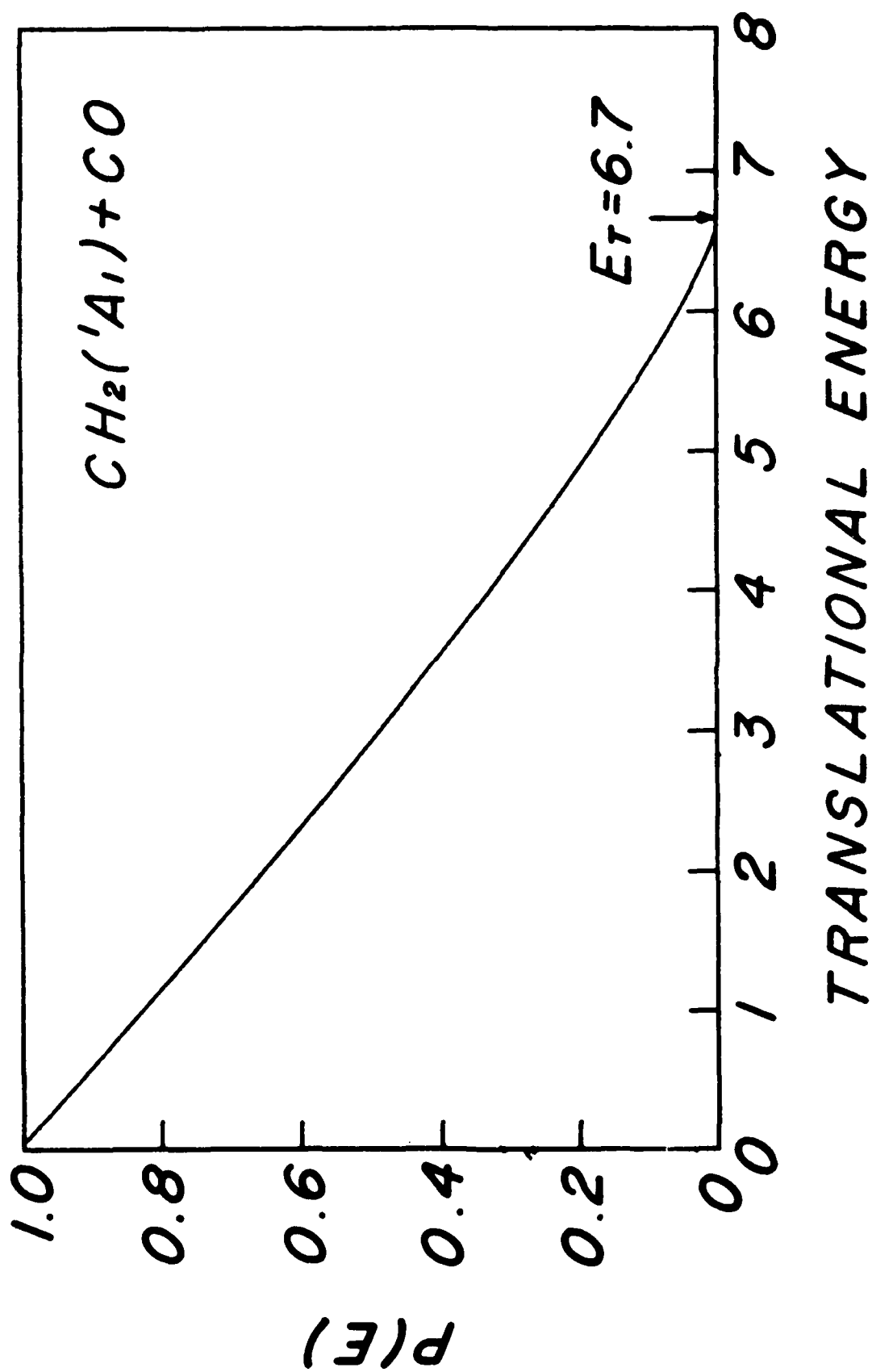
Fig. 4



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Fig. 5





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Fig. 6

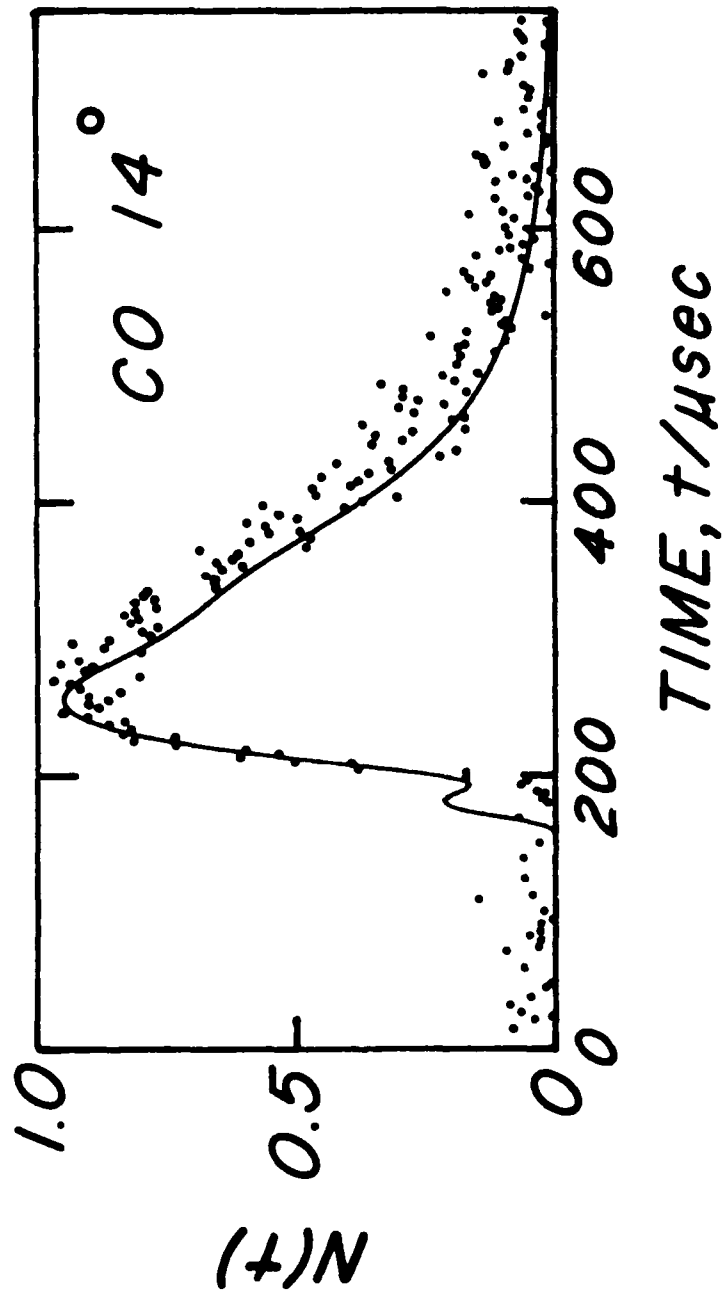


Fig. 7

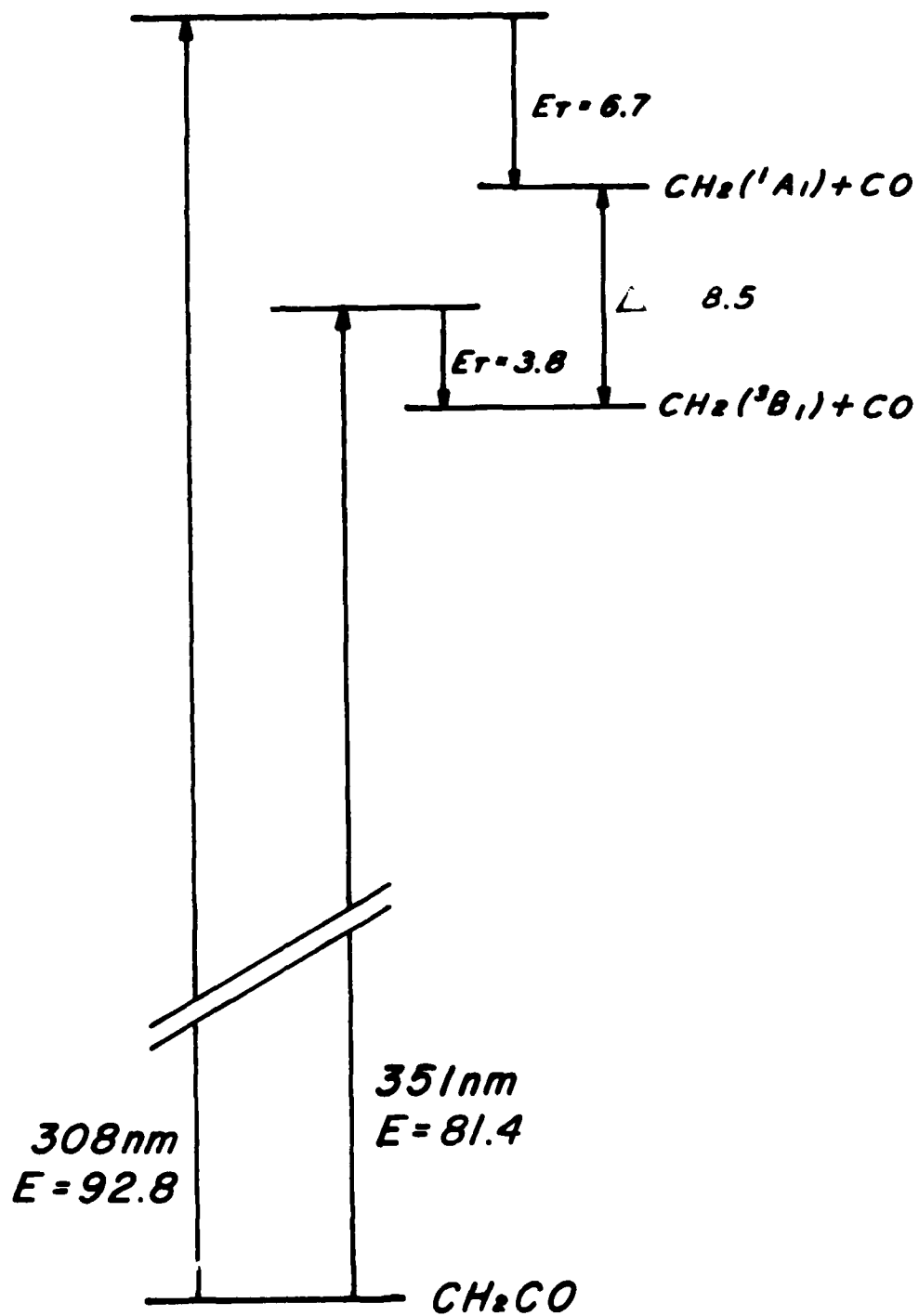


Fig. 8

D. State Distribution of Photodissociation Products of O_3 .

Guo-zhong He, R. J. Sparks, H. S. Kwok, and Y. T. Lee

The purpose of this work was to investigate the laser-frequency dependence of product state distributions of the ozone photolysis. Important questions which need to be answered about the photodissociation of ozone are the variation of branching ratio between $O_2(^3\Sigma_g^-)$ and $O_2(^1\Delta_g)$ and the vibrational state distributions of $O_2(^1\Delta_g)$ as a function of photon energy.

High resolution molecular beam measurements of the translational velocity distribution of the primary photolysis products of ozone were carried out at 279 nm, 276 nm, 266 nm, 259 nm, and 248 nm. Identification of product quantum states and their population distributions are obtained from the analysis of time-of-flight velocity spectra.

The molecular beam machine used for this experiment and the method for data processing and analysis have been described in detail.^{1,2} Experiments were carried out by crossing a supersonic molecular beam of ozone seeded in argon at a right angle with the laser beam of various frequencies; a frequency quadrupled pulsed Nd:YAG laser for 266 nm, a frequency doubled pulsed dye laser for 279 nm, 276 nm, and 259 nm, and an excimer laser for 248 nm.

The energy diagram of $O + O_2$ and photon energies of the five laser wavelengths used are shown in Fig. 1. Product state distributions obtained for these laser wavelengths are shown in Table 1. The relative

population of different vibrational states in $O_2(^1\Delta_g)$ for five laser wavelengths are shown in Table 2.

From the experimental results, we concluded:

1. $O_2(^3\Sigma_g^-)$ production was found to be around 10% in the frequency range covered. It increased slightly (~1-2%) as the laser wavelength decreased from 279 nm to 248 nm.
2. The vibrational state distribution of $O_2(^1\Delta_g)$ obeys approximately the Boltzmann distribution, and the vibrational temperature of $O_2(^1\Delta_g)$ increases as the photon energy increases. Approximate vibrational temperatures are 2700°K and 3500°K at 266 nm and 259 nm respectively.

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Table 1. Product State Distributions for the Five Laser Wavelengths.

Laser Wavelength State	279 (nm)	276 (nm)	266 (nm)	259 (nm)	248 (nm)
$O_2(^1\Sigma_g^-)$	12.2%	12.2%	11.6%	11.5%	10.4%
$O_2(^1\Delta_g)_{v=0}$	57.6%	53.1%	50.3%	42.1%	37.9%
$v=1$	25.2%	25.5%	23.9%	23.0%	28.3%
$v=2$	5.0%	9.2%	9.7%	11.5%	10.4%
$v=3$			4.5%	7.7%	5.2%
$v=4$				4.2%	4.8%
$v=5$					3.0%

Table 2. The Relative Populations of Different Vibrational States in $O_2(^1\Delta_g)$ for the Five Laser Wavelengths.

<u>Laser Wavelength</u> State	279 (nm)	276 (nm)	266 (nm)	259 (nm)	248 (nm)
$O_2(^1\Delta_g)_{v=0}$	1.00	1.00	1.00	1.00	1.00
$v=1$	0.44	0.48	0.47	0.55	0.75
$v=2$	0.09	0.17	0.19	0.27	0.27
$v=3$			0.09	0.18	0.14
$v=4$				0.10	0.13
$v=5$					0.08

FIGURE CAPTION

Fig. 1. The energy diagram of $O + O_2$ and the photon energies.

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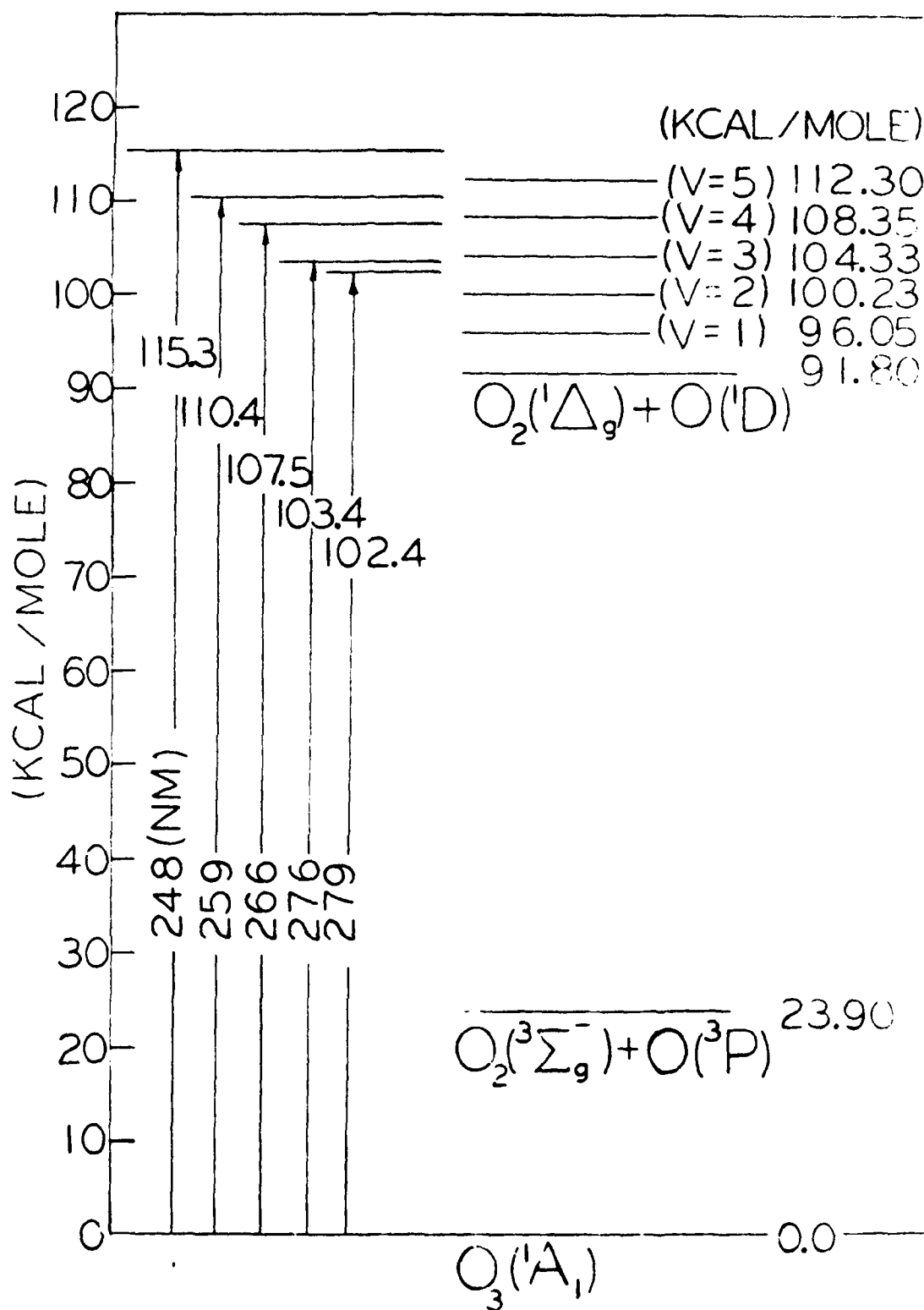


Fig. 1

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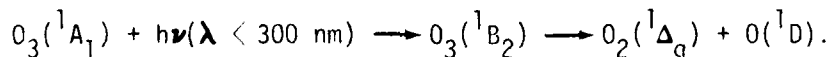
II. Publication of ONR Supported Research

A. Papers Published in 1980

1. Ozone Photolysis: A Determination of the Electronic and Vibrational State Distributions of Primary Products. R. K. Sparks, L. R. Carlson, K. Shobatake, M. L. Kowalczyk, and Y. T. Lee, J. Chem. Phys. 72, 1401 (1980).

ABSTRACT

We have undertaken recently several studies on the photodissociation dynamics of small molecules. Since photodissociation mechanisms are poorly understood for systems other than diatomics, we have chosen ozone as a suitable molecule to study. Extensive theoretical and spectroscopic efforts have been made by other workers which renders a base of information complimentary to our studies. The photolysis of ozone is important not only from a theoretical view but also as an important source of metastable $O(^1D)$ atoms in the atmosphere. The quantum efficiency for production of $O(^1D)$ has been estimated to be unity for the process.



We find, however, that there is an important contribution from previously unseen ground state products. We find at λ 266 nm a quantum efficiency for production of $O(^3P) + O_2(^3\Sigma_g^-)$ to be 12%. This neglected product channel can be significant in quantitative atmospheric modeling calculations.

2. Development of a Supersonic $O(^3P_J)$, $O(^1D_2)$ Atomic Oxygen Nozzle Beam Source. Steven J. Sibener, Richard J. Buss, Cheuk Yiu Ng, and Yuan T. Lee, Rev. Sci. Instr. 51, 167 (1980).

ABSTRACT

A high pressure, radio frequency discharge nozzle beam source has been developed for the production of very intense ($\sim 10^{18}$ atoms $\text{sr}^{-1} \text{sec}^{-1}$) supersonic beams of oxygen atoms. An efficient impedance matching scheme has been devised for coupling the radio frequency power to oxygen-rare gas mixtures as a function of gas pressure, temperature, and composition. Techniques for localizing the discharge directly behind the orifice of a specially designed quartz nozzle have also been developed. The above combine to yield a beam source which reliably produces a high degree of molecular dissociation in oxygen-rare gas mixtures at pressures

up to 350 torr. Atomic oxygen mean translational energies from 0.14 - 0.50 eV have been achieved using the seeded beams technique with Mach numbers up to 10 being realized. When helium is used as the carrier gas both $O(^3P_J)$ and $O(^1D_2)$ atoms are present in the beam, while only ground state atoms appear to be present in argon seeded mixtures. This paper describes the design, construction, and operation of this beam source and provides a characterization of the atomic oxygen beams it has reproducibly generated in our laboratory.

3. A Crossed Molecular Beams Investigation of the Reactions $O(^3P) + C_6H_6$, C_6D_6 . Steven J. Sibener, Richard J. Buss, Piergiorgio Casavecchia, Tomohiko Hirooka, and Yuan T. Lee, J. Chem. Phys. 72, 4341 (1980).

ABSTRACT

A crossed beam investigation of the reactions of $O(^3P) + C_6H_6$, C_6D_6 has been carried out using a seeded, supersonic, atomic oxygen nozzle beam source. Angular and velocity distributions of reaction products have been used to identify the major reaction pathways. The initially formed triplet biradical, C_6H_6O (C_6D_6O), either decays by hydrogen (deuterium) elimination or becomes stabilized, most likely by nonradiative transition to the S_0 manifold of ground state phenol. CO elimination was not found to be a major channel. The branching ratio between H(D) atom elimination and stabilization was found to be sensitive to both collision energy and isotopic substitution.

4. Observation of CH_3O Product in the Crossed Beam Study of the $O(^1D) + CH_4$ Reaction. P. Casavecchia, R. J. Buss, S. J. Sibener, and Y. T. Lee, J. Chem. Phys. 73, 6351 (1980).

ABSTRACT

The reaction of $O(^1D)$ and CH_4 is understood to proceed along two distinct pathways: a) by insertion of $O(^1D_2)$ into the C-H bond to form "hot" methanol, which fragments in the absence of stabilizing collisions; and b) by abstraction of H atoms to form OH and CH_3 radicals. Uncertainty remains as to how the "hot" methanol decompose. It is suggested that in addition to form CH_3 and OH by breaking C-H bond, the other important channel is the elimination of H_2 forming H_2CO . In this crossed molecular beams studies, it is shown that the formation of $H_2 + H_2CO$ is in fact negligible in comparison with the more important channel, $CH_3O + H$.

B. Paper Submitted for Publication

1. On the Photodissociation of Nitromethane at 266 nm. H. S. Kowk, G. Z. He, R. K. Sparks, and Y. T. Lee, Int. J. Chem. Kinet. (1981) in press.

ABSTRACT

In a crossed laser-molecular beam study of nitromethane, it was found that the excitation of nitromethane at 266 nm did not yield dissociation products under collision free conditions. When a small cluster of nitromethane was excited at the same frequency, product was seen only at energies and masses consistent with rupture of the van der Waals bond by vibrational predissociation of the excited state.

C. Invited Lectures presented during the contract period.

1. Y. T. Lee, "Reaction of Oxygen Atoms with Unsaturated Hydrocarbons," Harvard-MIT Joint Physical Chemistry Seminar, Cambridge, Massachusetts, March 13, 1980.
2. Y. T. Lee, "Dynamics of Photodissociation of O_3 ," XI Informal Conference on Photochemistry, Newport Beach, California, March 30 - April 3, 1980.
3. Y. T. Lee, "Reaction of Oxygen Atoms with Unsaturated Hydrocarbons," Department of Chemistry, Columbia University (Falk-Plaut Lectures) April 16, 1980.
4. Y. T. Lee, "Dynamical Resonances in State-to-State Chemical Reactions," Department of Chemistry, Columbia University (Falk-Plaut Lectures) April 17, 1980.
5. Y. T. Lee, "Dynamics of the Reactions of Oxygen Atoms with Unsaturated Hydrocarbons," Naval Research Laboratory, Washington, D.C., April 24, 1980.
6. Y. T. Lee, "Infrared Multiphoton Dissociation of Polyatomic Molecules," Department of Chemistry, University of Nevada, Reno, Nevada, May 9, 1980.
7. Y. T. Lee, "Reaction of Oxygen Atoms with Unsaturated Hydrocarbons," Department of Chemistry, California Institute of Technology, Pasadena, California, May 21, 1980.
8. Y. T. Lee, "Photodissociation of Molecules by High Power Lasers," Eyring Symposium, University of Utah, Salt Lake City, Utah, June 13, 1980.

9. Y. T. Lee, "Lecture series on Chemical Kinetics and Reaction Dynamics," Institute of Chemistry, Beijing, China, June 23 - July 12, 1980.
10. Y. T. Lee, "Lecture series on Molecular Beam Chemical Kinetics," Institute of Chemical Physics, Dalian, China, July 16-20, 1980.
11. Y. T. Lee, "Photofragmentation Translational Spectroscopy of Ozone and Methyl Iodide," Institute of Optics, Shanghai, China, July 22, 1980.
12. Y. T. Lee, "Dynamics of Infrared Multiphoton Dissociation of Polyatomic Molecules," Shanghai Science Association, Shanghai, China, July 23, 1980.
13. Y. T. Lee, "Reaction of Oxygen Atoms with Unsaturated Hydrocarbons," Fudan University, China, July 24, 1980.
14. Y. T. Lee, "Reaction Mechanism of Oxygen Atoms with Unsaturated Hydrocarbons," Chinese University of Hong Kong, July 30, 1980.
15. Y. T. Lee, "Energy Splitting Between Singlet and Triplet Methylene," Department of Chemistry, University of California, Berkeley, California, September 30, 1980.
16. Y. T. Lee, "Photodissociation of Ketene: Singlet-Triplet Energy Splitting of Methylene," Joint Physics and Chemistry Department Colloquium, University of Oregon, Eugene, Oregon, November 6, 1980.
17. Y. T. Lee, "Recent Advances of Photofragmentation Translational Spectroscopy," Western Spectroscopy Association Conference, Asilomar, Pacific Grove, California, January 28-30, 1981.
18. Y. T. Lee, "Dynamics of Infrared Multiphoton Dissociation of Polyatomic Molecules," Lawrence Livermore Laboratory, Livermore, California, March 11, 1981.
19. Y. T. Lee, "Crossed Molecular Beam Studies of Elementary Atomic and Molecular Processes," Lester Kuhn Memorial Lecture, Department of Chemistry, Johns Hopkins University, Baltimore, Maryland, March 17, 1981.
20. Y. T. Lee, "Recent Advances of Molecular Beam Chemistry, Department of Chemistry, Pennsylvania State University, College Station, Pennsylvania, March 19, 1981.

II. Research Programs for April 1, 1981 to March 30, 1982.

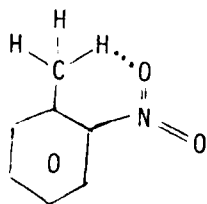
The research program in the forthcoming year will be mainly concerned with the dynamics of the unimolecular dissociation of polyatomic molecules. The isolated molecules will be energized by either an IR multiphoton excitation process or using single UV photon excitation. The IR multiphoton excitation process will enable us to study the decomposition in the ground electronic state and the UV excitation will allow us to investigate the dissociation through electronic excitation. The investigation of the same molecule using two different excitation processes is very useful in elucidating the nature of the dissociation process.

The method which will be applied in these studies is molecular beam photofragmentation translational spectroscopy. Information on primary products and the detailed dissociation dynamics will be obtained from the mass spectrometric measurements of velocity and angular distributions of primary products using an universal crossed molecular beams apparatus.

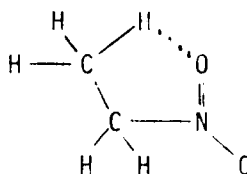
Two types of compounds, namely aliphatic nitrocompounds and aromatic nitrocompounds will be investigated in the coming year. In both of these two types of compounds, the understanding of the dissociation mechanism and identification of primary dissociation products are one of our first goals.

In both aliphatic and aromatic nitrocompounds, one would expect that the simple C-N bond rupture forming NO_2 and radical molecules

should be an important channel, but it is not well understood whether the formation of HONO through a cyclic transition state such as

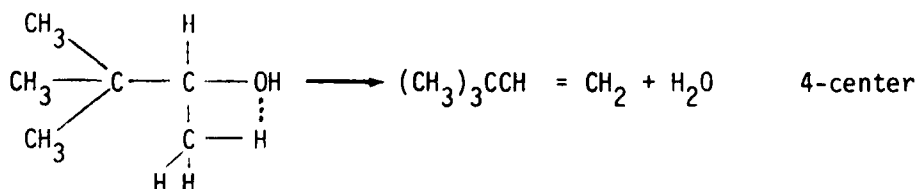


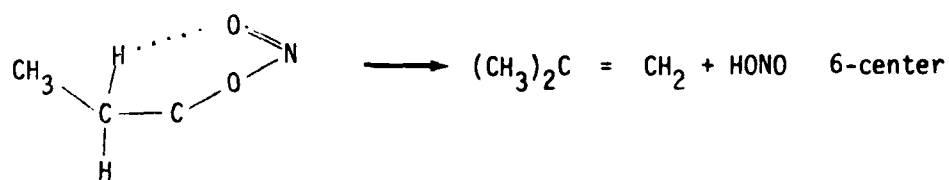
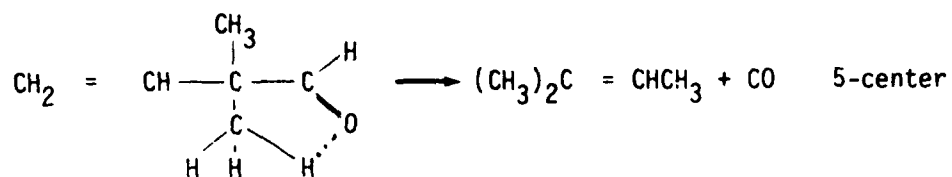
and



plays an important role in the decomposition of these nitrocompounds. We will attempt to study the decomposition of ortho-meta and para toluene as well as nitromethane, nitroethane and nitropropane systematically. In our recent study of vinyl ethyl ether, we did find that the products formed through the cyclic transition state released on the average 30 kcal/mole as translational. Such a high translational energy release is certainly not expected.

In order to understand the unimolecular decomposition which goes through the cyclic transition state, we will also study a series of reactions which are known to decompose through 4, 5, 6 center eliminations. For example,





will be studied concurrently with nitrocompounds for comparison.

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